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(54) Title of the Invention: SILICON NITRIDE BASED SINTERED BODY

(57) Abstract

PURPOSE: To provide a silicon nitride based sintered body having excellent oxidation resistance characteristics along with maintaining the conventional strength characteristics of silicon nitride.

CONSTITUTION: A sintered body obtained by molding and firing a mixture containing, as a sintering aid, 1-10 wt % ytterbium oxide, 0.2-10 wt % hafnium oxide, and 1-10 wt % aluminum nitride, with the remainder essentially composed of silicon nitride. The parent phase of the silicon nitride based sintered body is composed of  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, or  $\beta$ -Si<sub>3</sub>N<sub>4</sub> and  $\alpha'$ -Si<sub>3</sub>N<sub>4</sub>. The grain boundary of the sintered body parent phase contains at least a crystalline complex oxide containing Yb and Hf.

## [Claims]

### [Claim 1]

A silicon nitride based sintered body, wherein a mixture containing, as a sintering aid, 1–10 wt % ytterbium oxide, 0.2–10 wt % hafnium oxide, and 1–10 wt % aluminum nitride, with the remainder essentially composed of silicon nitride, is molded and fired.

### [Claim 2]

A silicon nitride based sintered body, wherein the sintered body parent phase is composed of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> or  $\beta$ -Si<sub>3</sub>N<sub>4</sub> and  $\alpha'$ -Si<sub>3</sub>N<sub>4</sub>, and at least a crystalline complex oxide containing Yb and Hf is present in the grain boundary of the sintered body parent phase.

## [Detailed Description of the Invention]

### [0001]

#### [Industrial Field of Application]

The present invention relates to a silicon nitride based sintered body having excellent oxidation resistance.

### [0002]

Heretofore, silicon nitride based sintered bodies, silicon carbide based sintered bodies, sialon based sintered bodies comprising mainly the constituent elements of Si-Al-O-N, etc., have been used as structural materials for ceramic systems. Among these, silicon nitride based sintered bodies have higher strength than silicon carbide based sintered bodies and sialon based sintered bodies, as well as having characteristics such as a superior fracture toughness value, and application thereof has been attempted in various high-strength, heat-resistant structural materials beginning with materials for automotive parts, gas turbine blades, and the like.

### [0003]

In this connection, since the sintering properties of silicon nitride itself are extremely poor, in the past various sintering methods have been attempted, and at present high density sintering by means of additives is mainly used. High density sintering by means of these additives (sintering aids) is a process whereby a liquid phase is formed in the grain boundaries by adding a metallic compound having a lower melting point than silicon nitride, and a dense silicon nitride sintered body is obtained by facilitating the realignment and phase transition of the silicon nitride granules by means of this liquid phase.

[0004]

Oxides of rare earth elements, aluminum oxide, aluminum nitride, and other oxides, carbides, silicides, etc., of hafnium, tantalum, and niobium can be cited as compounds which function as sintering aids for silicon nitride, and these may be used alone or combinations. Known combinations of these sintering aids include, for example, yttrium oxide–aluminum oxide–aluminum nitride–oxide of hafnium, tantalum, niobium, etc. types (see Japanese Examined Patent Application Publication No. Hei 1-16791), rare earth oxide–oxide of hafnium, tantalum, niobium, etc. or rare earth oxide–oxide of hafnium, tantalum, niobium, etc.–aluminum nitride types (see Japanese Laid-open Patent Application Publication No. Sho 60-290718), and others.

[0005]

[Problems That the Invention Is to Solve]

Nevertheless, silicon nitride based sintered bodies which use the aforementioned sintering aids have a problem that, since a dense sintered body is obtained by forming a liquid phase during firing and facilitating the realignment and phase transition of granules by means of this liquid phase, the constituents which form the liquid phase remain in the crystal boundaries after sintering, and oxidation resistance is impaired mainly due to the aforesaid intergranular structural phase. More specifically, while mainly yttrium oxide is used as a sintering aid, silicon nitride sintered bodies in which yttrium oxide is used, due to the intergranular phase containing yttrium, are especially susceptible to oxidation at high temperatures, and have the problem of degradation of strength when used in a high temperature atmosphere.

[0006]

As stated above, while yttrium oxide which is used as a sintering aid for silicon nitride is able to produce a silicon nitride based sintered body having good density and excellent mechanical strength, due to the compounds containing yttrium which remain in the granule boundaries after sintering, it has a problem of degraded oxidation resistance. Therefore a process which allows a silicon nitride based sintered body to be obtained having excellent oxidation resistance characteristics without a significant reduction in sintered body density or mechanical strength has been strongly desired.

[0007]

The present invention was produced as a solution to this problem and has the object of offering a silicon nitride based sintered body having excellent oxidation resistance.

[0008]

[Means Used to Solve the Problems and Operation]

The silicon nitride based sintered body of the present invention is characterized in that a mixture containing, as a sintering aid, 1–10 wt % ytterbium oxide, 0.2–10 wt % hafnium oxide, and 1–10 wt % aluminum nitride, with the remainder essentially composed of silicon nitride, is molded and fired. The silicon nitride sintered body of the present invention is also characterized in that the sintered body parent phase is composed of  $\beta$ - $\text{Si}_3\text{N}_4$ , or  $\beta$ - $\text{Si}_3\text{N}_4$  and  $\alpha'$ - $\text{Si}_3\text{N}_4$ , and at least a crystalline complex oxide containing Yb and Hf is present in the grain boundary of the sintered body parent phase.

[0009]

The silicon nitride which forms the main material of the silicon nitride based sintered body the present invention should have an average particle diameter of 1  $\mu\text{m}$  or less and have at least 80% of the structural phase as the  $\alpha$ -phase. The sintered body parent body produced by this silicon nitride material is composed mainly of  $\beta$ - $\text{Si}_3\text{N}_4$  phase as a structural phase, and may also contain  $\alpha'$ - $\text{Si}_3\text{N}_4$  phase in a ratio of 20% or less.

[0010]

The ytterbium oxide used as the sintering aid in the present invention functions as a sintering promoter for silicon nitride, and remains as a crystalline compound having a high melting point in the grain boundaries after sintering. Here, the crystalline compound containing Yb remaining in the grain boundaries is formed together with hafnium oxide, which also serves mainly as a sintering aid, and the crystalline complex oxide containing Yb and Hf may be, for example,  $\text{Yb}_6\text{HfO}_{11}$ .

[0011]

The aforesaid Yb-Hf based complex oxide is stable when exposed to high temperature atmospheres, has little movement of atoms, and can increase the oxidation resistance of the silicon nitride based sintered body. In a silicon nitride based sintered body which uses yttrium oxide as a sintering aid, for example, the Y in the grain boundary component can easily move in the surface direction, impairing the oxidation resistance characteristics of the sintered body. In the silicon nitride based sintered body of the present invention, since oxidation accompanying the movement of the grain boundary constituents as described above is prevented, good oxidation resistance characteristics can be maintained even in high temperature atmospheres.

[0012]

The additive amount of ytterbium oxide should be in a range of 1–10 wt %, preferably 2–7 wt %, of the total composition. If the additive amount of ytterbium oxide is less than 1 wt %, then the sintering promotion function is insufficient, and it exceeds 10 wt %, then the ratio of the parent phase will be relatively lowered, so that it will be difficult to obtain the original characteristics of the sintered body. As the material for the ytterbium oxide, a compound such as a silicide, carbide, or boride which forms an oxide when heated may be used.

[0013]

Hafnium oxide functions as a sintering promoter for silicon nitride, forming a complex oxide together with Yb, as described above, and prevents the degradation of oxidation resistance

characteristics of the silicon nitride based sintered body. Depending upon the additive amount of each sintering aid, a portion of the hafnium oxide by itself may be present in the crystal boundary, but since hafnium oxide also has excellent high temperature strength, etc., there is no reduction in the oxidation resistance characteristics or high temperature strength. The additive amount of such hafnium oxide should be in a range of 0.2–10 wt %, preferably 0.3–3 wt %, of the total composition. When the additive amount of hafnium oxide is less than 0.2 wt %, the sintering promotion function cannot be sufficiently obtained, and when it exceeds 10 wt %, the ratio of the parent phase will be relatively lowered, so that it will be difficult to obtain the original characteristics of the sintered body. As the material for the hafnium oxide, a compound such as a silicide, carbide, or boride which forms an oxide when heated may be used.

[0014]

Aluminum nitride, which is another sintering aid constituent in the present invention, assists the sintering promotion effect of the ytterbium oxide and hafnium oxide, promotes liquid phase sintering of the silicon nitride, and also contributes to the recrystallization of the liquid phase that has been formed. However, if the additive amount is too great, the amount remaining in the crystal boundaries increases, so the additive amount should be no more than 10 wt %. Moreover, since it is difficult to form a liquid phase if the amount added is too small, the additive amount should be at least 1 wt %. Preferably, the additive amount of hafnium nitride should be in a range of 2–7 wt %.

[0015]

The total amount of the constituents added as these sintering aids should be in a range of 4–20 wt % of the total composition. If the total additive amount is less than 4 wt %, then the effect of promoting liquid phase sintering will be insufficient, and the amount exceeds 20 wt %, the probability of impairment of the basic characteristics of silicon nitride is increased.

[0016]

The silicon nitride based sintered body of the present invention can be obtained by molding into a desired shape a blend containing the aforesaid constituents in ratios within the specified range, and

firing said mixture in an inert atmosphere in a temperature range of 1600°C–1900°C. In sintering, a silicon nitride based sintered body having good density and excellent oxidation resistance characteristics can also be obtained by means of a so-called normal pressure sintering process, but the sintered body having similar qualities can also be obtained using other sintering processes, e.g., an atmosphere compression sintering process, hot press process, hot isostatic sintering process (HIP), and the like.

[0017]

[Working Examples]

The present invention is explained below by means of working examples.

[0018]

Working Example 1

5 wt %  $\text{Yb}_2\text{O}_3$  powder having an average particle diameter of 1.0  $\mu\text{m}$ , 2 wt %  $\text{HfO}_2$  powder having an average particle diameter of 1.1  $\mu\text{m}$ , and 4 wt %  $\text{AlN}$  powder having an average particle diameter of 1.0  $\mu\text{m}$  were blended with  $\text{Si}_3\text{N}_4$  ( $\alpha$ -phase 95%) powder having an average particle diameter of 0.8  $\mu\text{m}$ , and the material powder was prepared by mixing for approximately 24 hours using a ball mill. Next, 5 wt parts of a binder was added and blended per 100 wt parts of this material powder, and after thorough mixing, a rod-shaped molded body 50 mm long  $\times$  50 mm wide  $\times$  7 mm thick was formed by press molding.

[0019]

Next, after degreasing treatment was performed on the aforesaid molded body in a nitrogen gas atmosphere, normal pressure sintering was performed at 1770°C for 2 hrs in a nitrogen gas atmosphere, and a sintered body composed mainly of silicon nitride was obtained.

[0020]

When the structural phases of the silicon nitride based sintered body thus obtained were analyzed by an X-ray diffraction apparatus, the 88% comprising the parent phase was the  $\beta$ - $\text{Si}_3\text{N}_4$  phase,

and the remaining 12% was  $\alpha'$ - $\text{Si}_3\text{N}_4$  phase. The main crystal phase of the intergranular phase was  $\text{Yb}_6\text{HfO}_{11}$ .

[0021]

As a comparison with the present invention, a sintered body was prepared under the same conditions as Working Example 1, using a material powder in which 5 wt %  $\text{Yb}_2\text{O}_3$  powder (average particle diameter 0.9  $\mu\text{m}$ ), 2 wt %  $\text{HfO}_2$  powder, and 4 wt %  $\text{AlN}$  powder were blended with  $\text{Si}_3\text{N}_4$  ( $\alpha$ -phase 95%) powder used in Working Example 1.

[0022]

The three-point bending strength of the aluminum nitride sintered bodies of the working example and comparative example was measured at room temperature and at 1250°C. Further, heat treatment was performed on these sintered bodies in air at 1400°C for 100 hours, and after treatment the oxidation amount (weight increase) per unit area of sample was calculated. Additionally, the three-point bending strength at room temperature was measured for these test pieces after heat treatment. The results are shown in Table 1.

[0023]

[Table 1]

	Three-point bending strength (Mpa)		After heat treatment at 1400°C for 100 hrs	
	Room temp.	1250°C	Oxidation wt increase (mg/cm <sup>2</sup> )	Three-point bending strength (Mpa)
Working Example 1	860	730	0.3	760
Comparative Example 1	980	800	> 1.0	250

As is clear from the measurement results shown in Table 1, the silicon nitride based sintered body obtained in Working Example 1 has slightly poorer strength than the sintered body of the comparative example, which uses  $\text{Y}_2\text{O}_3$  as a sintering aid, but has superior oxidation resistance,



and greatly superior strength compared to the sintered body of the comparative example after heat treatment.

[0024]

#### Working Examples 2-5

The  $\text{Yb}_2\text{O}_3$  powder,  $\text{HfO}_2$  powder, and  $\text{AlN}$  powder used in Working Example 1 were blended with  $\text{Si}_3\text{N}_4$  powder in the ratios shown in Table 2, and using these material powders, sintering was performed on the same conditions as in Working Example 1, and silicon nitride based sintered bodies were prepared.

[0025]

The physical properties of the silicon nitride sintered bodies obtained in this way were measured in the same way as in Working Example 1. The results are also shown in Table 2.

[0026]

[Table 2]

		Added constituents (wt % in total composition)			Three-point bending strength (Mpa)		After heat treatment at 1400°C for 100 hrs	
		$\text{Yb}_2\text{O}_3$	$\text{HfO}_2$	$\text{AlN}$	Room temp.	1250°C	Oxidation wt increase (mg/cm <sup>2</sup> )	Three-point bending strength (Mpa)
Wkg Ex	2	9	2	4	870	700	0.3	720
	3	3	2	3	780	680	0.3	760
	4	5	1	4	800	700	0.3	730
	5	9	3	7	770	650	0.3	690

[0027]

#### [Effects of the Invention]

As explained above, the silicon nitride based sintered body of the present invention, in addition to maintaining the conventional strength characteristics of silicon nitride, also provides excellent oxidation resistance characteristics. Accordingly, it is possible to offer a ceramic type material that

is suitable as a structural material for various uses in high temperature atmospheres.

[0028]

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